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The spin-unrestricted molecular Kohn–Sham solution and the analogue of Koopmans’s theorem for open-shell molecules

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Spin-unrestricted Kohn–Sham (KS) solutions are constructed from accurate *ab initio* spin densities for the prototype doublet molecules NO₂, ClO₂, and NF₂ with the iterative local updating procedure of van Leeuwen and Baerends (LB). A qualitative justification of the LB procedure is given with a “strong” form of the Hohenberg–Kohn theorem. The calculated energies $\varepsilon_{i\sigma}$ of the occupied KS spin orbitals provide numerical support to the analogue of Koopmans’ theorem in spin-density functional theory. In particular, the energies $-\varepsilon_{i\beta}$ of the minor spin (β) valence orbitals of the considered doublet molecules correspond fairly well to the experimental vertical ionization potentials (VIPs) I_i^1 to the triplet cationic states. The energy $-\varepsilon_{H\alpha}$ of the highest occupied (spin-unpaired) α orbital is equal to the first VIP I_H^0 to the singlet cationic state. In turn, the energies $-\varepsilon_{i\alpha}$ of the major spin (α) valence orbitals of the closed subshells correspond to a fifty-fifty average of the experimental VIPs I_i^1 and I_i^0 to the triplet and singlet states. For the Li atom we find that the exact spin densities are represented by a spin-polarized Kohn–Sham system which is not in its ground state, i.e., the orbital energy of the lowest unoccupied β spin orbital is lower than that of the highest occupied α spin orbital (“a hole below the Fermi level”). The addition of a magnetic field in the $-z$ direction will shift the β levels up so as to restore the Aufbau principle. This is an example of the nonuniqueness of the mapping of the spin density on the KS spin-dependent potentials discussed recently in the literature. The KS potentials may no longer go to zero at infinity, and it is in general the differences $\nu_{s\sigma}(\infty) - \varepsilon_{i\sigma}$ that can be interpreted as (averages of) ionization energies. In total, the present results suggest the spin-unrestricted KS theory as a natural one-electron independent-particle model for interpretation and assignment of the experimental photoelectron spectra of open-shell molecules. © 2004 American Institute of Physics.

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I. INTRODUCTION

Open-shell molecules present a more challenging task for photoelectron spectroscopy than closed-shell ones and only relatively few photoelectron spectra were reported in the literature for open-shell systems. Prominent among them are the prototype doublet molecules NX₂ ($X = \text{O, F}$) (Refs. 1 and 2) and ClO₂,³ which are of importance for interstellar spectra and atmospheric chemistry. The open-shell spectra are complicated with ionization to states of different spin, in particular, for doublet molecules these are singlet and triplet ionic states with the corresponding vertical ionization potentials (VIPs) I_i^0 and I_i^1 .

Furthermore, theoretical photoelectron spectroscopy of open-shell systems lacked a one-electron independent-particle approach to assign VIPs comparable with Koopmans’ theorem⁴ of the Hartree–Fock (HF) theory for closed-shell molecules. The latter identifies the energies ε_i^{HF} of the occupied HF orbitals ϕ_i^{HF} as approximate VIPs of the primary ionization $I_i^{1/2}(\phi_i^{-1})$ to the doublet ionic states. Primary ionizations are those that can be described in good approximation by a Koopmans configuration, i.e., a single orbital ionization. No comparable assignment for VIPs I_i^0 and I_i^1 of doublet molecules has been made so far.

This situation can be changed radically with the analogue of Koopmans’s theorem for spin-density functional

theory (SDFT) established recently in Ref. 5. It provides the physical meaning for the energies $\varepsilon_{i\sigma}$ of the Kohn–Sham spin orbitals $\phi_{i\sigma}$ in the one-electron equations

$$\{-\frac{1}{2}\nabla^2 + \nu_{s\sigma}(\mathbf{r}_1)\}\phi_{i\sigma}(\mathbf{r}_1) = \varepsilon_{i\sigma}\phi_{i\sigma}(\mathbf{r}_1), \quad (1.1)$$

$$\rho_{\sigma}(\mathbf{r}_1) = \sum_i^{N_{\sigma}} |\phi_{i\sigma}(\mathbf{r}_1)|^2, \quad (1.2)$$

where $\nu_{s\sigma}$ are the spin-unrestricted KS potentials and ρ_{σ} are the exact spin densities [the summation in Eq. (1.2) goes over the lowest occupied $\phi_{i\sigma}$]. The SDFT analogue of Koopmans’ theorem is based on the exact relations between $\varepsilon_{i\sigma}$ and VIPs. In the case of doublet open-shell systems considered in this paper the ε - I relations connect the energy $\varepsilon_{i\beta}$ of the occupied minor spin β orbital to the multitude $\{I_j^1\}$ of VIPs from an N electron doublet ground state $\Psi_0^{N,1/2}$ to $(N-1)$ electron triplet states $\Psi_j^{(N-1),1}$

$$\varepsilon_{\beta} = -\mathbf{M}_{\beta}^{-1}\mathbf{P}_{\beta}^1\mathbf{I}^1 + \mathbf{M}_{\beta}^{-1}\varepsilon_{\beta}^{\text{resp}}. \quad (1.3)$$

In its turn, VIPs $\{I_j^0\}$ and $\{I_j^1\}$ to both singlet $\Psi_j^{(N-1),0}$ and triplet $\Psi_j^{(N-1),1}$ states determine the energy $\varepsilon_{i\alpha}$ of the occupied major spin α orbital

$$\varepsilon_{\alpha} = -\mathbf{M}_{\alpha}^{-1}\mathbf{P}_{\alpha}^0\mathbf{I}^0 - \mathbf{M}_{\alpha}^{-1}\mathbf{P}_{\alpha}^1\mathbf{I}^1 + \mathbf{M}_{\alpha}^{-1}\varepsilon_{\alpha}^{\text{resp}}. \quad (1.4)$$

In Eqs. (1.3) and (1.4) \mathbf{M}_σ is the $(N_\sigma \times N_\sigma)$ matrix of the weighted overlap between the densities of the KS orbitals, $M_{kj}^\sigma = \int |\phi_{k\sigma}(\mathbf{r}_1)|^2 |\phi_{j\sigma}(\mathbf{r}_1)|^2 / \rho_\sigma(\mathbf{r}_1) d\mathbf{r}_1$, while $\mathbf{P}_\sigma^{S'}$ is the analogous $(N_\sigma \times \infty)$ matrix for the KS and Dyson orbitals $d_{j\sigma}$, $P_{kj\sigma}^{S'} = \int |\psi_{k\sigma}(\mathbf{r}_1)|^2 \times |d_{j\sigma}(\mathbf{r}_1)|^2 / \rho_\sigma(\mathbf{r}_1) d\mathbf{r}_1$, where $d_{j\sigma}$ is the “generalized overlap amplitude”⁶ of overlap between $\Psi_0^{N,1/2}$ and $\Psi_j^{(N-1),S'}$

$$d_{j\sigma}(\mathbf{r}_1)\sigma(s_1) = \sqrt{N} \int \Psi_j^{(N-1),S'}(\mathbf{x}_2, \dots, \mathbf{x}_N) \times \Psi_0^{N,1/2}(\mathbf{x}_1, \dots, \mathbf{x}_N) d\mathbf{x}_2 \cdots d\mathbf{x}_N. \quad (1.5)$$

The infinite-dimensional column vectors \mathbf{I}^0 and \mathbf{I}^1 contain all the corresponding ionization energies, which are ordered in the same way as the set of Dyson orbitals (i.e., the columns of \mathbf{P}_σ^0 and \mathbf{P}_σ^1), namely the primary ionizations come first. In all cases considered in this study it is possible to identify just one ionization as a primary one corresponding to a particular β orbital or the spin-unpaired α orbital and two primary ionizations corresponding to a spin-paired α orbital of the closed subshell. The N_σ -dimensional column vector $\boldsymbol{\varepsilon}_\sigma^{\text{resp}}$ contains the matrix elements $\varepsilon_{j\sigma}^{\text{resp}} = \int |\phi_{j\sigma}(\mathbf{r}_1)|^2 \nu_{\text{resp},\sigma}(\mathbf{r}_1) d\mathbf{r}_1$ of the “response” potential for the occupied KS orbitals.⁷ In Ref. 5 the ε - I relations of the type (1.3), (1.4) were derived also for the higher spin $S > 1/2$ for the KS solution, which represents the spin densities corresponding to the “top” component Ψ_0^{NSS} of the multiplet $\{\Psi_0^{NSM}\}$ of degenerate states of the interacting system with spin S . The problem with the DFT description of entire degenerate spin multiplets, which was not considered in Ref. 5, is well known and was, for instance, addressed in Refs. 8 and 9.

The qualitative interpretation of Eqs. (1.3) and (1.4) made in Ref. 5 allows us to identify the minor spin KS orbital energies $\varepsilon_{i\beta}$ with primary ionizations to the triplet states

$$\varepsilon_{i\beta} \approx -I^1(\varphi_i^{-1}), \quad (1.6)$$

while the major spin energies $\varepsilon_{i\alpha}$ of spin-paired α orbitals of the closed subshell are represented with a fifty-fifty mixture of primary ionizations to the singlet and triplet states

$$\varepsilon_{i\alpha} \approx -\frac{1}{2}I^0(\varphi_i^{-1}) - \frac{1}{2}I^1(\varphi_i^{-1}). \quad (1.7)$$

For the highest occupied β spin molecular orbital (β HOSMO) $\phi_{H-1,\beta}$, Eq. (1.6) becomes an exact identity, while the energy of the unpaired α HOSMO $\phi_{H\alpha}$ is exactly equal to the potential of ionization to the singlet ground state of the $(N-1)$ electron system

$$\varepsilon_{H\alpha} = -I^0(\varphi_H^{-1}). \quad (1.8)$$

In this paper we shall assess the quality of the SDFT analogue (1.6)–(1.8) of Koopmans’s theorem, which has been derived theoretically in Ref. 5, with the construction of the spin-unrestricted KS solution from accurate (*ab initio*) spin densities ρ_σ for prototype open-shell molecules. Previously, to our best knowledge, only rather accurate spin-restricted KS solutions were reported for closed-shell molecules.^{10–13}

The KS solution is constructed in this paper with the spin-unrestricted extension of the iterative local updating procedure of van Leeuwen and Baerends¹⁴ (LB) for the molecules NO_2 , ClO_2 , NF_2 as well as for the Li atom. In Sec. II the spin-unrestricted LB procedure is presented within the context of a “strong” form of the Hohenberg–Kohn¹⁵ (HK) theorem. In Sec. III the KS spin-orbital energies $\varepsilon_{i\alpha}$ and $\varepsilon_{i\beta}$ obtained for NO_2 , ClO_2 , and NF_2 are compared with the experimental VIPs $I^0(\phi_i^{-1})$ and $I^1(\phi_i^{-1})$ obtained from photoelectron spectra. The comparison is also made with the orbital energies of the generalized gradient approximation (GGA) and of the unrestricted Hartree–Fock (UHF) method. The calculated KS energies $\varepsilon_{i\alpha}$ and $\varepsilon_{i\beta}$ are shown to be in a fair agreement with their Koopmans’-type estimates, Eqs. (1.6) and (1.7). In Sec. IV a peculiar spin-unrestricted KS (UKS) solution is obtained for the Li atom, which illustrates nonuniqueness of the KS potentials in SDFT. In Sec. V the conclusions are drawn and the implications of the presented results for SDFT and theoretical electron spectroscopy are made.

II. SPIN-UNRESTRICTED VAN LEEUWEN AND BAERENDS PROCEDURE

The spin-unrestricted extension of the LB procedure constructs the KS solutions (1.1) from the *ab initio* spin densities ρ_α and ρ_β obtained with the configuration interaction (CI) method. In this paper ρ_α and ρ_β have been produced from the CI total density $\rho = \rho_\alpha + \rho_\beta$ and spin-polarization density $\sigma = \rho_\alpha - \rho_\beta$ calculated by means of the ATMOL package.¹⁶ The construction of the KS solution has been performed with a Gaussian orbital density functional code¹⁷ based on the ATMOL package. The iterative LB procedure starts from some initial potential $\nu_{s\sigma}^0$ and updates the current potential $\nu_{s\sigma}^i(\mathbf{r})$ at each point \mathbf{r} of the numerical grid using the difference $\Delta\rho_\sigma = \rho_\sigma(\mathbf{r}) - \rho_\sigma^i(\mathbf{r})$ of the target CI spin density and the spin density $\rho_\sigma^i(\mathbf{r})$ obtained from Eq. (1.2) for the current KS solution.

The mechanism behind the LB procedure can be understood with a “strong” form of the HK theorem applied to the noninteracting KS system. In this case the canonical HK theorem¹⁵ may be succinctly stated as asserting that when some change $\Delta\nu_{s\sigma}$ is made to the KS potential of Eq. (1.1), there must ensue a density change $\Delta\rho_\sigma$ (we use the spin labels $\sigma = \alpha, \beta$, but the whole argument is taken over unmodified from the spin-restricted case). The theorem can be put in a stronger form, however, in the following way. Consider two KS potentials $\nu_{s\sigma}^{(1)}$ and $\nu_{s\sigma}^{(2)}$ with their difference $\Delta\nu_{s\sigma} = \nu_{s\sigma}^{(2)} - \nu_{s\sigma}^{(1)}$, the corresponding ground state KS determinants $\Psi_s^{(1)} = \det\{\phi_{i\sigma}^{(1)}(\mathbf{r}_i)\sigma(s_i)\}$ and $\Psi_s^{(2)} = \det\{\phi_{i\sigma}^{(2)}(\mathbf{r}_i)\sigma(s_i)\}$ with the densities $\rho_\sigma^{(1)}$ and $\rho_\sigma^{(2)}$, and the density difference $\Delta\rho_\sigma = \rho_\sigma^{(2)} - \rho_\sigma^{(1)}$. We assume that the potentials $\nu_{s\sigma}^{(2)}$ and $\nu_{s\sigma}^{(1)}$ differ by more than a uniform constant. Then, we have from the variation theorem that

$$\begin{aligned}
& -\frac{1}{2} \sum_{i=1}^{N_\sigma} \int \phi_{i\sigma}^{(2)*}(\mathbf{r}) \nabla^2 \phi_{i\sigma}^{(2)}(\mathbf{r}) d\mathbf{r} + \int \rho_\sigma^{(2)}(\mathbf{r}) \nu_{s\sigma}^{(1)}(\mathbf{r}) d\mathbf{r} \\
& > -\frac{1}{2} \sum_{i=1}^{N_\sigma} \int \phi_{i\sigma}^{(1)*}(\mathbf{r}) \nabla^2 \phi_{i\sigma}^{(1)}(\mathbf{r}) d\mathbf{r} \\
& + \int \rho_\sigma^{(1)}(\mathbf{r}) \nu_{s\sigma}^{(1)}(\mathbf{r}) d\mathbf{r}.
\end{aligned} \quad (2.1)$$

Similarly, we have

$$\begin{aligned}
& -\frac{1}{2} \sum_{i=1}^{N_\sigma} \int \phi_{i\sigma}^{(1)*}(\mathbf{r}) \nabla^2 \phi_{i\sigma}^{(1)}(\mathbf{r}) d\mathbf{r} + \int \rho_\sigma^{(1)}(\mathbf{r}) \nu_{s\sigma}^{(2)}(\mathbf{r}) d\mathbf{r} \\
& > -\frac{1}{2} \sum_{i=1}^{N_\sigma} \int \phi_{i\sigma}^{(2)*}(\mathbf{r}) \nabla^2 \phi_{i\sigma}^{(2)}(\mathbf{r}) d\mathbf{r} \\
& + \int \rho_\sigma^{(2)}(\mathbf{r}) \nu_{s\sigma}^{(2)}(\mathbf{r}) d\mathbf{r}.
\end{aligned} \quad (2.2)$$

Adding these two inequalities yields

$$\int \Delta \rho_\sigma(\mathbf{r}) \Delta \nu_{s\sigma}(\mathbf{r}) d\mathbf{r} < 0. \quad (2.3)$$

One can therefore state that more is known than that a change $\Delta \nu_{s\sigma}$ must induce some change $\Delta \rho_\sigma$ or (because of the invertible mapping from the set of the KS potentials to the set of the densities) vice versa. It follows from Eq. (2.3) that a negative change $\Delta \rho_\sigma$ will correspond, predominantly, to a repulsive change $\Delta \nu_{s\sigma}$ in the corresponding region, while a positive change $\Delta \rho_\sigma$ will correspond, predominantly, to an attractive change $\Delta \nu_{s\sigma}$. A striking illustration is provided in Fig. 2(d) of Ref. 18, where it is shown that oscillations of the density of an approximate Kohn–Sham system around the exact density correspond precisely to oscillations of the approximate KS potential around the exact one. The $\Delta \rho$ and $\Delta \nu$ oscillations have opposite phase, but go through zero at the same points.

In the LB procedure the assumption is made [in accordance with Eq. (2.3)] that if there is locally a deviation $\Delta \rho_\sigma(\mathbf{r}) = \rho_\sigma(\mathbf{r}) - \rho_\sigma^i(\mathbf{r})$ of the density ρ_σ^i (resulting from a trial potential $\nu_{s\sigma}^i$) from the target CI density ρ_σ , then we may apply a local update $\Delta \nu_{s\sigma}(\mathbf{r})$ to the potential $\nu_{s\sigma}^i(\mathbf{r})$ in the direction opposite to $\Delta \rho_\sigma(\mathbf{r})$ in order to obtain an improved potential. In the current variant of the LB procedure $\nu_{s\sigma}$ is decomposed into the fixed external potential ν_{ext} and the Hartree potential ν_{Coul} (Ref. 19) of the electrostatic electron repulsion of the target density ρ , and the unknown exchange–correlation (xc) potential $\nu_{xc\sigma}$. Only the latter relatively small potential is updated as follows:

$$\Delta \nu_{s\sigma}(\mathbf{r}) = \Delta \nu_{xc\sigma}(\mathbf{r}) = \frac{\Delta \rho_\sigma(\mathbf{r})}{\rho_\sigma^i(\mathbf{r})} \nu_{xc\sigma}^i(\mathbf{r}). \quad (2.4)$$

Since $\nu_{xc\sigma}$ is an attractive (negative) potential, Eq. (2.4) produces a local potential change $\Delta \nu_{s\sigma}(\mathbf{r})$ of the opposite sign to $\Delta \rho_\sigma(\mathbf{r})$, so that the integral condition (2.3) of the “stronger” form of the HK theorem is fulfilled in the LB procedure for the deviation $\Delta \rho_\sigma$ from the target CI density. Besides, the correct Coulombic asymptotics $-1/r$ together with the requirements (1.6) and (1.8) for the HOSMOs are imposed on $\nu_{xc\sigma}$ within the LB scheme, as was described in

Refs. 18 and 20. In practice it turns out that a certain amount of damping in Eq. (2.4) accelerates the convergence if one iterates to obtain a rather accurate KS potential. An essentially similar updating procedure to obtain KS potentials from given densities has been applied by Nagy.²¹ The results of the spin-unrestricted LB procedure will be presented in the next section.

A tacit assumption in the above has been that the local Kohn–Sham potential corresponding to the given density ρ does exist. It has been argued^{22–25} that such a potential indeed will always exist, or at least that a local potential can be constructed whose corresponding Kohn–Sham density approaches the target density arbitrarily closely. These arguments for the total density and spin-restricted Kohn–Sham potential carry over unmodified to the separate spin densities ρ_σ and potentials $\nu_\sigma(\mathbf{r})$, where each spin potential is determined up to a constant. We will return below to some consequences of the existence of *two* undetermined constants in the spin-unrestricted case.

III. $\varepsilon_{i\sigma}$ OF SPIN-UNRESTRICTED KOHN–SHAM POTENTIALS VERSUS EXPERIMENTAL VIPs

The spin-orbital energies $\varepsilon_{i\alpha}$ and $\varepsilon_{i\beta}$ obtained with the spin-unrestricted LB procedure for the doublet molecules NO_2 , ClO_2 , and NF_2 are presented in Tables I–III. They are compared, according to the SDFT analogue of Koopmans’ theorem (1.6)–(1.8), with the experimental singlet and triplet valence VIPs I^0 and I^1 determined with UV photoelectron spectroscopy.^{1–3} A comparison is also made with $\varepsilon_{i\sigma}$ calculated with the spin-unrestricted potentials of a standard SDFT GGA, the combination BP of the exchange functional of Becke,²⁶ (B88), and the correlation functional of Perdew²⁷ (P86), as well as with $\varepsilon_{i\sigma}$ of the UHF method. The CI spin densities ρ_σ and the subsequent spin-unrestricted KS solutions (1.1) and (1.2) have been obtained with the correlation-consistent polarized core-valence quadruple-zeta (aug-cc-pcVQZ) basis sets²⁸ of contracted Gaussian functions for the second-row-element molecules NO_2 and NF_2 with all *f*, *g*, and the most diffuse *d* functions excluded. For ClO_2 similar triple-zeta correlation-consistent valence (cc-pVTZ) basis sets^{29,30} have been used. The same basis sets have been used for the BP and UHF calculations.

The calculated valence KS energies $\varepsilon_{i\sigma}$ agree fairly well with their SDFT-Koopmans estimate (1.6)–(1.8) from the experimental VIPs. First, we consider the minor spin β -orbital energies $\varepsilon_{i\beta}$, which, according to Eq. (1.6), are identified with the pure potentials of the primary ionization $I^1(\phi_i^{-1})$. The most remarkable result is the close correspondence between $\varepsilon_{i\beta}$ and $I^1(\phi_i^{-1})$ for NO_2 (see Table I) with an average deviation of only 0.05 eV. For ClO_2 (Table II) the deviation between $I^1(\phi_i^{-1})$ and $-\varepsilon_{i\beta}$ increases with the orbital energy, going from 0.28 eV for the $1a_2\beta$ orbital energy, $\varepsilon_{H-2,\beta} = -12.71$, to 0.92 eV for $1a_2\beta$, $\varepsilon_{H-5,\beta} = -16.95$, and for $7a_1\beta$ $\varepsilon_{H-6,\beta}$ jumps to 2 eV (see Table II). For NF_2 (Table III) only the two first triplet VIPs $I^1(\phi_i^{-1})$ have been reported in Ref. 2, and with the condition $\varepsilon_{H-1,\beta} = -I^1(\phi_{H-1}^{-1})$ imposed on the $6a_1\beta$ HOSMO energy, the energy $\varepsilon_{H-2,\beta}$ of the next β orbital, $4b_2\beta$, differs from $I^1(\phi_{H-2}^{-1})$ by 1.27 eV.

TABLE I. Orbital energies $-\varepsilon_{i\sigma}$ (eV) of the spin-unrestricted KS (UKS) and GGA-BP (UBP) calculations for the NO₂ molecule compared with the experimental VIPs. The last column contains the experimental VIPs and the column “Eqs. (1.6) and (1.7)” cites the experimental VIPs to the triplet states $I^1(\phi_i^{-1})$, to be compared with $-\varepsilon_{i\beta}$, and the average of the experimental VIPs [$I^0(\phi_i^{-1}) + I^1(\phi_i^{-1})/2$], to be compared with $-\varepsilon_{i\alpha}$. The column “UBP” contains in parentheses (and italicized) for the highest UBP orbital energies $\varepsilon_{6a1,\alpha}$ and $\varepsilon_{4b2,\beta}$ the downshift required to bring them in agreement with the exact KS orbital energies. For the other UBP orbital energies the downshifted values (with these amounts) are shown in parentheses.

$-\varepsilon_{i\sigma}$		UHF	UBP	UKS	Experiment	
					Eqs. (1.6) and (1.7)	VIPs (Ref. 1)
$6a_1$	α	13.75	6.60(4.65)	11.25	11.25	11.25(¹ A ₁)
$4b_2$	β	13.54	8.53(4.49)	13.02	13.02	13.02(³ B ₂)
	α	16.29	9.17(13.82)	13.87	13.77	14.52(¹ B ₂)
$1a_2$	β	14.36	9.38(13.87)	13.48	13.60	13.60(³ A ₂)
	α	14.45	9.53(14.18)	14.04	13.83	14.07(¹ A ₂)
$1b_1$	β	20.43	13.42(17.91)	17.40	17.45	17.45(³ B ₁)
	α	20.93	14.29(18.94)	18.61	17.61	17.77(¹ B ₁)
$5a_1$	β	19.57	13.87(18.36)	17.96	18.00	18.00(³ A ₁)
	α	22.85	14.36(19.01)	19.11	19.60	21.2 (¹ A ₁)
$3b_2$	β	20.70	14.09(18.58)	18.13		
	α	22.01	14.30(18.95)	18.86		
$4a_1$	β	24.15	16.31(20.62)	20.38		
	α	26.48	16.74(21.39)	21.48		
$2b_2$	β	39.80	28.50(32.99)	32.86		
	α	40.94	28.93(33.58)	33.69		
$3a_1$	β	44.71	32.36(36.85)	36.56		
	α	45.88	32.74(37.39)	37.48		
$2a_1$	β	431.53	387.13(391.62)	392.30		
	α	432.16	387.37(392.02)	393.09		
$1b_2$	β	562.56	513.59(518.08)	518.51		
	α	562.95	513.81(518.46)	518.77		
$1a_1$	β	562.56	513.59(518.08)	518.51		
	α	562.95	513.81(518.46)	518.77		

We turn now to the major spin α -orbital energies $\varepsilon_{i\alpha}$ which are identified with the fifty-fifty mixtures (1.7) of potentials of the primary ionization to singlet $I^0(\phi_i^{-1})$ and triplet $I^1(\phi_i^{-1})$ states. The deviations are typically larger than for the spin β orbital energies, though still reasonably small. This is already apparent from the α -orbital energies $\varepsilon_{i\alpha}$ of NO₂ in Table I, which deviate on average 0.36 eV from experiment, to be compared to the 0.05 deviation for the β orbital energies mentioned above. A fair agreement is also observed between the 5 lowest (next to $\varepsilon_{H\alpha}$) orbital energies $-\varepsilon_{i\alpha}$ of ClO₂ and [$I^0(\phi_i^{-1}) + I^1(\phi_i^{-1})$]/2 (see Table II). The average deviation of the calculated 6 lowest energies $\varepsilon_{i\alpha}$ of ClO₂ from its SDFT–Koopmans estimate is 0.24 eV. The next orbital energy, $\varepsilon_{7a1,\alpha}$, however, exhibits a deviation of ca. 2 eV, just as the energy $\varepsilon_{7a1,\beta}$ of the corresponding spin-paired β orbital considered above. In the case of NF₂ the experimental value [$I^1(6a_1^{-1}) + I^0(6a_1^{-1})$]/2 = 15.49 eV agrees well with the calculated value $\varepsilon_{6a1,\alpha} = 15.26$ eV (see Table III).

Table III exhibits a peculiar trend for the energies of the spin-paired α and β orbitals of the closed subshells of NF₂. The point is that, in general, the SDFT–Koopmans relations (1.5) and (1.6) predict lower energy for the α orbital compared to that of the spin-paired β orbital. This is so, since the α -orbital energy (1.6) has an admixture of the VIP $I^0(\phi_i^{-1})$ to a singlet state, which is presumably higher than the VIP $I^1(\phi_i^{-1})$ to the corresponding triplet state. The inequality $I^1(\phi_i^{-1}) < I^0(\phi_i^{-1})$ holds true for all experimental VIPs in

Tables I–III and, in agreement with Eqs. (1.5) and (1.6), the calculated α -orbital energies of the closed subshells are lower than the corresponding β -orbital energies for all orbitals of NO₂ and ClO₂ (see Tables I and II) as well as for the $6a_1$, $1b_1$, $5a_1$, and $4a_1$ MOs of NF₂ (see Table III). However, for other MOs of NF₂ the calculated β -orbital energies are somewhat lower than the energies of the spin-paired α orbitals.

This reversed order of α and β orbitals as well as larger deviations of some of the calculated KS energies from their SDFT–Koopmans VIPs estimates are due to the approximate nature of the latter. Indeed, while Eqs. (1.6) and (1.7) identify $\varepsilon_{i\sigma}$ just with VIPs of corresponding primary ionizations, the exact ε – I relations (1.3),(1.4) contain also contributions from other ionizations as well as from the response potential. The results of this section indicate that these other contributions tend to cancel each other for outer valence orbitals. Still, in some cases this cancellation might not be complete, and from our previous closed-shell calculations^{20,31} we can expect that this will be especially true for the deep valence and core orbitals.

The BP orbital energies in Tables I–III display the well-known feature of the GGA xc potentials, that they are not attractive enough, especially in the bulk molecular region. Due to this, GGA systematically underestimates (in absolute value) the KS orbital energies. For α and β HOSMOs the corresponding upward shifts ($\varepsilon_{H\alpha}^{BP} + I_H^0$) and ($\varepsilon_{H-1,\beta}^{BP} + I_{H-1}^1$), which are placed in parentheses (italicized) in the

TABLE II. Orbital energies $-\varepsilon_{i\sigma}$ (eV) of the spin-unrestricted KS (UKS) and GGA-BP (UBP) calculations for the ClO_2 molecule compared with the experimental VIP's. The last column contains the experimental VIP's and the column "Eqs. (1.6) and (1.7)" cites the experimental VIPs to the triplet states $I^1(\phi_i^{-1})$, to be compared with $-\varepsilon_{i\beta}$, and the average of the experimental VIPs $[I^0(\phi_i^{-1}) + I^1(\phi_i^{-1})]/2$, to be compared with $-\varepsilon_{i\alpha}$. The column "UBP" contains in parentheses (and italicized) for the highest UBP orbital energies $\varepsilon_{3b1,\alpha}$ and $\varepsilon_{8a1,\beta}$ the downshift required to bring them in agreement with the exact KS orbital energies. For the other UBP orbital energies the downshifted values (with these amounts) are shown in parentheses.

$-\varepsilon_{i\sigma}$		UHF	UBP	UKS	Experiment	
					Eqs. (1.6) and (1.7)	VIPs (Ref. 3)
$3b_1$	β	10.70				
	α	10.95	6.15(4.32)	10.47	10.47	10.47(1A_1)
$8a_1$	β	12.37	8.38(4.21)	12.59	12.59	12.59(3B_1)
	α	15.07	8.64(12.96)	13.33	12.61	12.63(1B_1)
$1a_2$	β	16.04	8.46(12.67)	12.71	12.99	12.99(3B_2)
	α	16.75	9.47(13.79)	13.86	14.21	15.44(1B_2)
$5b_2$	β		8.46(12.67)	12.79	13.33	13.33(3A_2)
	α	17.53	8.67(12.99)	13.41	13.46	13.59(1A_2)
$2b_1$	β	20.01	12.93(17.14)	16.70	17.30	17.30(3A_1)
	α	20.11	13.35(17.67)	17.61	17.44	17.58(1A_1)
$4b_2$	β	19.70	12.90(17.11)	16.95	17.87	17.87(3A_2)
	α	20.27	13.18(17.50)	17.79	17.96	18.06(1A_2)
$7a_1$	β	17.56	13.14(17.35)	17.06	19.06	19.06(3B_1)
	α	21.03	13.68(18.00)	18.04	19.78	20.50(1B_1)
$6a_1$	β	26.41	18.00(22.21)	21.88		
	α	27.62	18.55(22.87)	23.00		
$3b_2$	β	37.23	25.57(29.78)	30.87		
	α	39.57	26.94(31.26)	31.60		
$5a_1$	β	41.74	30.26(34.47)	34.28		
	α	42.91	30.55(34.87)	35.05		
$2b_2$	β	222.84	195.66(199.87)	201.51		
	α	222.78	195.85(200.17)	203.26		
$1b_1$	β	222.98	195.84(200.05)	202.11		
	α	222.79	195.88(200.20)	203.79		
$4a_1$	β	223.00	196.01(200.22)	202.44		
	α	222.96	196.05(200.37)	204.06		
$3a_1$	β	291.91	255.22(259.43)	261.26		
	α	291.81	255.28(259.60)	263.15		
$1b_2$	β	561.52	512.13(516.34)	521.83		
	α	562.17	512.36(516.68)	522.71		
$2a_1$	β	561.52	512.13(516.34)	521.83		
	α	562.17	512.36(516.68)	522.71		
$1a_1$	β	2857.54	2747.60(2751.81)	2755.30		
	α	2857.47	2747.67(2751.99)	2761.72		

HOSMO rows of Tables I–III, are close to each other for a particular molecule. They range from 4.32 and 4.21 eV for ClO_2 to 5.23 and 5.04 eV for NF_2 , respectively. Addition of these shifts to other orbital energies shows the systematic nature of the deviations of the BP orbital energies from the KS ones in the sense that the shifted energies in parentheses in the BP columns of Tables I–III are rather close to the corresponding KS energies with differences which, as a rule, do not exceed 0.5 eV. This indicates the good quality of the shape of the unrestricted BP potentials in the valence region.

An interpretation of the upward shift of the GGA orbital energies has been proposed in the literature, which is based on the KS theory of systems with a fractional number of particles.^{32–34} According to this interpretation, the xc potential of standard GGAs for an N electron system averages over the upward discontinuity jump Δ of the KS potential when the number of electrons in the KS system changes from $N - \omega$ to $N + \omega$, $\omega \rightarrow 0$.^{34,35} Then, the spin-restricted KS (RKS) approach applied to an open-shell system yields for its single

RKS xc potential the discontinuity jump $\Delta = I_H^0 - A$, where A is the electron affinity of the system.³² This jump lines up the highest occupied orbital energy, which is $\varepsilon_H = -I_H^0$ at N electrons, with the electron affinity $-A$, which is equal to ε_H for $N + \omega$, up to $N + 1$.

While the total density $\rho = \rho_\alpha + \rho_\beta$ of an open-shell system can in principle be reproduced correctly with a single KS potential, equal for α and β spin electrons, the individual spin densities ρ_α and ρ_β would not be correct in that case. In this respect, RKS can be viewed as only an approximation for open-shell systems, an adequate description requiring spin-unrestricted KS (UKS) theory, as considered in this paper. In UKS, however, one should consider not a single, but two discontinuity jumps Δ_α and Δ_β of its potentials (1.1). In the UKS theory for systems with a fractional number of particles, which will be presented elsewhere, the α potential $\nu_{xc\alpha}$ jumps upwards (as the number of particles changes from $N - \omega$ to $N + \omega$) by $\Delta_\alpha = -A - \varepsilon_{H\alpha}$ (which is equal to

TABLE III. Orbital energies $-\varepsilon_{i\sigma}$ (eV) of spin-unrestricted KS (UKS) and GGA-BP (UBP) calculations for the NF_2 molecule compared with the experimental VIPs. The last column contains the experimental VIPs and the column “Eqs. (1.6) and (1.7)” cites the experimental VIPs to the triplet states $I^1(\phi_i^{-1})$, to be compared with $-\varepsilon_{i\beta}$, and the average of the experimental VIPs $[I^0(\phi_i^{-1}) + I^1(\phi_i^{-1})]/2$, to be compared with $-\varepsilon_{i\alpha}$. The column “UBP” contains in parentheses (and italicized) for the highest UBP orbital energies $\varepsilon_{6a1,\alpha}$ and $\varepsilon_{4b2,\beta}$ the downshift required to bring them in agreement with the exact KS orbital energies. For the other UBP orbital energies the downshifted values (with these amounts) are shown in parentheses.

$-\varepsilon_{i\sigma}$		UHF	UBP	UKS	Experiment	
					Eqs. (1.6) and (1.7)	VIPs (Ref. 2)
$2b_1$	α	15.00	6.87(5.23)	12.10	12.10	12.10(1A_1)
$6a_1$	β	15.83	9.56(5.04)	14.60	14.60	14.60(3B_1)
	α	16.63	9.97(15.20)	15.26	15.49	16.38(1B_1)
$4b_2$	β	18.27	10.50(15.54)	16.33	17.6	17.6 (3A_2)
	α	18.23	10.58(15.81)	15.98		
$1a_2$	β	18.46	10.93(15.97)	17.10		
	α	19.75	11.38(16.61)	16.40		
$1b_1$	β	20.11	12.81(17.85)	18.50		
	α	22.89	13.54(18.77)	18.83		
$5a_1$	β	21.47	13.29(18.33)	18.77		
	α	21.72	13.54(18.99)	18.85		
$3b_2$	β	21.81	15.12(20.16)	20.14		
	α	21.92	15.33(20.56)	20.09		
$4a_1$	β	28.28	19.60(24.64)	24.64		
	α	30.85	20.36(25.59)	25.45		
$2b_2$	β	44.55	31.12(36.16)	36.99		
	α	44.75	31.32(36.55)	36.62		
$3a_1$	β	46.92	33.40(38.44)	39.03		
	α	47.56	33.72(38.95)	38.93		
$2a_1$	β	429.82	386.19(391.23)	392.92		
	α	430.87	386.68(391.91)	392.59		
$1b_2$	β	717.64	662.63(667.67)	668.77		
	α	717.73	662.73(667.96)	668.21		
$1a_1$	β	717.64	662.63(667.67)	668.77		
	α	717.73	662.73(667.96)	668.21		

the $\Delta = I_H^0 - A$ of the spin-restricted case), while the jump of the β potential $\nu_{xc\beta}$ is $\Delta_\beta = -A - \varepsilon_{H\beta}$, where $\varepsilon_{H\beta}$ is the energy of the lowest unoccupied β spin orbital (β LUSMO) $\phi_{H\beta}$. These α and β jumps are equal only in the RKS approximation, in which the α HOSMO and β LUSMO are degenerate, so that $\varepsilon_{H\beta} = \varepsilon_{H\alpha} = -I_H^0$. However, $\varepsilon_{H\beta}$ of the UKS solution for a doublet system can differ appreciably from $\varepsilon_{H\alpha}$ and Table IV illustrates this point comparing $-\varepsilon_{H\beta}$ with $-\varepsilon_{H\alpha} = I_H^0$ for NO_2 , NF_2 as well as for one of the simplest doublet systems, the Li atom (for all three systems there are also available the experimental electron affinities A , which are presented in Table IV). For our prototype molecules NO_2 and NF_2 the β LUSMO is considerably higher than the α HOSMO, which makes Δ_β considerably smaller than Δ_α . A surprising reverse situation takes place for Li, where the β LUSMO $\varepsilon_{H\beta}$ is somewhat lower than the

corresponding $\varepsilon_{H\alpha}$, the α HOSMO. The corresponding peculiar KS solution will be discussed in the next section.

According to the interpretation of Refs. 34 and 35, an upward shift $\Delta_\sigma^{\text{GGA}}$ of the GGA potential $\nu_{xc\sigma}^{\text{GGA}}$, which is a continuous function of $N \pm \omega$, could, at N , possibly be half of the abovementioned discontinuity jump of the KS potential $\nu_{xc\sigma}$ at N . In that case the GGA potential would be wrong at this point, yielding a too high (not negative enough) highest occupied orbital energy and hence a too slow asymptotic decay of the density, but it would then be equally wrong at $N - \omega$ (upshifted by $\Delta/2$) and at $N + \omega$ (downshifted by $\Delta/2$). In Table IV the “exact” half-jumps $\Delta_\alpha/2$ and $\Delta_\beta/2$ are compared with the evaluated upward shifts $\Delta\varepsilon_\alpha^{\text{BP}} = \varepsilon_{H\alpha}^{\text{BP}} - \varepsilon_{H\alpha}^{\text{KS}} = \varepsilon_{H\alpha}^{\text{BP}} + I_H^0$ and $\Delta\varepsilon_\beta^{\text{BP}} = \varepsilon_{H-1,\beta}^{\text{BP}} - \varepsilon_{H-1,\beta}^{\text{KS}} = \varepsilon_{H-1,\beta}^{\text{BP}} + I_{H-1}^1$ of the UBP one-electron energies of the highest occupied orbit-

TABLE IV. Discontinuity jumps $\Delta_\sigma = -A - \varepsilon_{H\sigma}$ (eV) of the spin-unrestricted Kohn–Sham (UKS) xc potentials going from N to $N + \delta$ electrons. The $\Delta_\sigma/2$ values are compared to the upward shifts $\Delta\varepsilon_\alpha^{\text{BP}} = \varepsilon_{H\alpha}^{\text{BP}} + I_H^0$ of the unrestricted GGA-BP (UBP) highest occupied α orbital energy and $\Delta\varepsilon_\beta^{\text{BP}} = \varepsilon_{H-1,\beta}^{\text{BP}} + I_{H-1}^1$ of the highest occupied β orbital energy, for NO_2 , NF_2 , and for the Li atom.

System	A	$I = -\varepsilon_{H\alpha}$	$-\varepsilon_{H\beta}$	$\Delta_\alpha/2$	$\Delta_\beta/2$	$\Delta\varepsilon_\alpha^{\text{BP}}$	$\Delta\varepsilon_\beta^{\text{BP}}$
NO_2	2.27	11.25	8.91	4.49	3.32	4.65	4.49
NF_2	1.21	12.10	8.63	5.44	3.71	5.23	5.04
Li	0.62	5.39	5.87	2.38	2.63	2.12	12.70

TABLE V. Orbital energies $-\varepsilon_{i\sigma}$ (eV) of the spin-unrestricted KS (UKS) and GGA-BP (UBP) solutions for the Li atom compared with the experimental VIPs.

$-\varepsilon_{i\sigma}$		UHF	UBP	UKS	Experiment	
					Eqs. (1.6) and (1.7)	VIPs (Ref. 37)
2s	β	0.04	2.29	5.87		
2s	α	3.50	3.27(2.12)	5.39	5.39	5.39($^1S(2s^{-1})$)
1s	β	68.84	51.71(12.7)	64.41	64.41	64.41($^3S(1s^{-1})$)
	α	68.88	51.90(54.02)	58.64	65.28	66.15($^1S(1s^{-1})$)

als of α and β spin, respectively, with respect to the exact values. The $\Delta\varepsilon_{\sigma}^{BP}$ values can be obtained directly from the BP spin-orbital energies and ionization energies presented in Tables I and III for NO_2 and NF_2 and Table V for Li. While the UBP α shifts $\Delta\varepsilon_{\alpha}^{BP}$ are in all cases reasonably close to the estimate $\Delta_{\alpha}/2$, with deviations in the order of a few tenths of an eV, this is not true for the UBP β shifts: $\Delta\varepsilon_{\beta}^{BP}$ is 1.17 eV larger (35.2%) than the corresponding $\Delta_{\beta}/2$ for NO_2 and for NF_2 it is 1.33 eV (35.8%) larger. For Li $\Delta\varepsilon_{\beta}^{BP}$ is 10.07 eV larger (483%) than $\Delta_{\beta}/2$. The assumption $\Delta\varepsilon_{\sigma}^{BP} \approx (-A - \varepsilon_{H\sigma}^{KS})/2$ is by no means obeyed quantitatively, and breaks down completely for Li. For Li this may be related to the fact that the $1s\beta$ belongs to the next lower shell and differs rather much in energy from $2s\beta$. Indeed, the BP potential $\nu_{xc\beta}^{BP}$ is certainly not uniformly shifted with respect to the KS potential. For instance, the upshift of the empty $2s\beta$ level of Li is $\varepsilon_{2s\beta}^{BP} - \varepsilon_{2s\beta}^{KS} = 3.58$, rather smaller than the 12.70 eV of the BP $1s\beta$, although still considerably larger than the $\Delta_{\beta}/2$ of 2.63 eV.

As was recognized in Refs. 34 and 36, the average over discontinuity of the KS potential is not a necessary condition for a continuous potential. Within SDFT, it is perfectly valid to construct a model KS potential that does not average over the discontinuity but represents the potential at the electron-deficient side and yields $\varepsilon_{H\alpha} = -I_H^0$ and $\varepsilon_{H-1,\beta} = -I_{H-1}^1$. If it is a continuous potential, in the sense that it changes continuously when a small fractional number ω is added to the system, it will deviate from the exact KS potential for the $N + \omega$ electron system. For finite systems like molecules, however, the KS potential for an $N + \omega$ electron system has limited usefulness. Such a fractional electron number KS system can only be given meaning as representing an ensemble of N and $N + 1$ electron systems. The KS potentials for such integer electron systems are physically meaningful and important for calculation and interpretation. Since no continuous potential can be right at both sides of the integer, or simultaneously at N and $N + \omega$ ($\omega \downarrow 0$), one might as well choose the electron-deficient side (equivalently, the integer-electron system).

Within the frozen orbital approximation and with the neglect of the electron Coulomb correlation, the Koopmans-type estimates (1.6)–(1.8) are also applicable to the orbital energies $\varepsilon_{i\sigma}^{HF}$ of UHF. However, this Hartree–Fock Koopmans-type estimate predicts the wrong first ionization for NO_2 and ClO_2 (see Tables I and II). While the SDFT Koopmans’s analogue correctly predicts the first ionization to be from the open-shell α orbital, this is not the case for NO_2 and ClO_2 . For NO_2 UHF agrees with UKS that the

unpaired α spin is in the $6a_1$ orbital, but the orbital energy of the $6a_1\alpha$ orbital proves to be below the $4b_2\beta$ orbital. So UHF predicts in the Koopmans frozen orbital approximation the first ionization to occur out of the β HOSMO, i.e., it predicts the lowest ion state to be a triplet. For ClO_2 the discrepancy of UHF with UKS and experiment is even more severe. The lowest energy in the UHF calculation corresponds to a configuration, where the highest level, the $3b_1$, is doubly occupied, and the unpaired α spin resides in an orbital ($5b_2$) that is not the highest one among the α orbitals, but the HOMO-4 (see Table II). The *Aufbau* principle is still not violated, since the corresponding $5b_2\beta$ orbital has an orbital energy -1.18 eV, which is much higher than the $5b_2\alpha$ orbital energy, and even higher than the orbital energy of the β HOSMO $3b_1\beta$. So both the α and the β spin orbital manifolds are occupied according to the *Aufbau* principle. However, the UHF Koopmans approximation leads to the estimate that the lowest state of the ion corresponds to ionization out of the $3b_1\beta$ orbital, i.e., to a triplet state of A_2 symmetry, in disagreement with experiment. The order of the β UHF spin orbitals is significantly distorted compared to the KS one, with $5b_2\beta$ completely out of line. The order of the α spin orbitals is the same in the two cases. Altogether, the UHF Koopmans-type estimate of the ionization energies consistently overestimates both triplet VIPs and the fifty-fifty average of the triplet and singlet VIPs (with the only exception of the lowest VIP to the triplet 3B_1 state of the ClO_2^+) and, in general, its accuracy is considerably worse than that of the SDFT Koopmans’ analogue (see Tables I–IV).

IV. A PECULIAR KOHN–SHAM SOLUTION FOR THE LI ATOM

A peculiar type of UKS solution is obtained for the Li atom. A rather large 5-zeta (cc-pV5Z) basis^{29,30} has been used for Li within the spin-unrestricted LB procedure of Sec. II and the calculated energies of the $1s$ and $2s$ spin orbitals are presented in Table V.

We generate the $\nu_{s\alpha}$ and $\nu_{s\beta}$ potentials with the constraint that they go to zero at infinity, in that case obtaining energies of the $2s\alpha$ and $1s\beta$ HOSMOs which represent the asymptotic decay of the α and β spin densities and are within our numerical accuracy equal to the experimental ionization energies according to conditions (1.6) and (1.7), $-\varepsilon_{2s\alpha} = I_H^0 = 5.39$ eV and $-\varepsilon_{1s\beta} = I_{H-1}^1 = 64.41$ eV (the experimental VIPs are taken from Ref. 37). It is to be noted that the $2s\beta$ LUSMO now appears to be lower by 0.48 eV than the $2s\alpha$ HOSMO (see Table V). Since $\varepsilon_{2s\beta} < \varepsilon_{2s\alpha}$, a change of

electron occupation, which removes an electron from the $2s\alpha$ HOSMO and places it in the $2s\beta$ LUSMO, produces a lower energy of this Kohn–Sham system of noninteracting electrons moving in the constructed KS potentials $\nu_{s\sigma}$. The total density and the spin densities will change upon this electron transfer. This appears to indicate that the exact (spin) density is not represented by the ground state of the KS system. The assumption (often called the Kohn–Sham ansatz) that always a local potential exists (or two local potentials in the spin-polarized case) such that the ground state of the noninteracting system reproduces the given exact density (or the exact spin densities), appears to break down in this case. We discuss below that this is not strictly true, although the situation we encounter here is inconvenient.

In the closed-shell spin-restricted case, the HK theorem establishes the one-to-one mapping of the scalar potentials $\nu(\mathbf{r})$ on densities $\rho(\mathbf{r})$. As a matter of fact, the densities determine the potential only up to a constant: $\rho(\mathbf{r}) \rightarrow \{\nu(\mathbf{r}) + C | C \in \mathfrak{R}\}$. We typically define the energy of the system as the difference between the ground state and the fully ionized system, i.e., the situation with all electrons removed to infinity and having zero kinetic energy. The constant in the potential adds CN to both the ground state and the ionized system, so it does not affect the energy. Applying the HK theorem to the noninteracting KS system, again the potential and hence the one-electron energies can be arbitrarily shifted by a constant. This does not invalidate the interpretation of the one-electron energies as related to ionization energies; one only has to take the asymptotic value of the potential, $\nu(\infty) = C$, into account: $I(\varphi_i^{-1}) \approx \nu(\infty) - \varepsilon_i$. It is convenient to always choose the natural gauge $\nu(\infty) = 0$. We note that addition of a constant to the KS potential does not interchange ground state and excited states of the KS system, since it shifts the orbital energies uniformly.

In the case of open-shell states of nonzero spin, one considers (as we have done in this paper) a potential that differentiates between spins, which is equivalent to a magnetic field acting on the electron spin [neglecting all other (relativistic) effects], and tries to establish a one-to-one mapping of the full 2×2 spin-density $\rho_{ss'}$ on the 2×2 potential matrix $w_{ss'}(\mathbf{r}) = \nu(\mathbf{r})\delta_{ss'} + g\mu_B\mathbf{B}(\mathbf{r}) \cdot \frac{1}{2}\sigma$ ($s = \alpha, \beta$), where g is the free electron g value, and μ_B is the Bohr magneton $e\hbar/2mc$. The freedom that in this case exists in the choice of the potentials $\nu(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$ has been carefully analyzed.^{38–40} We specialize in the case of collinear systems, i.e., eigenfunctions of \hat{S}_z with the magnetization vector at each point \mathbf{r} in the z direction: $\mathbf{m}(\mathbf{r}) = m(\mathbf{r})\hat{e}_z$. Our Kohn–Sham system with only pure α and β spin orbitals is of that type. For collinear systems there are two free constants, C and B , where C is the constant that can be added to the scalar potential $\nu(\mathbf{r})$, and B denotes the constant magnetic field in the z direction that can be added to $\mathbf{B}(\mathbf{r})$ without changing the wave function and the density. Adding the field $B\hat{e}_z$ does not change the Kohn–Sham orbitals but shifts the α one-electron levels up by $+g\mu_B B/2$ and the β levels down by $-g\mu_B B/2$. The fact that there are two free constants has peculiar consequences. Let us fix the zero of energy at the fully ionized system with N_α α electrons and N_β β electrons at infinity: $CN + (N_\alpha - N_\beta)g\mu_B B/2 = 0$. This does determine uniquely

the energy of the ground state of the system with this number of up spin and down spin electrons, which also changes with $CN + (N_\alpha - N_\beta)g\mu_B B/2$ when the scalar and magnetic potentials are varied with C and B . It does not determine the energy of other states of the system, with different numbers N'_α and N'_β of α and β electrons, respectively. With $CN = -\Delta N g\mu_B B/2$ from our choice of energy zero, the energy of the other state would change as $(\Delta N' - \Delta N)g\mu_B B/2$, where $\Delta N = N_\alpha - N_\beta$ and $\Delta N' = N'_\alpha - N'_\beta$. Evidently, variation of the B field can turn one or the other state into the ground state; see Refs. 38–40. So in the subspace of collinear systems, the requirement that the given spin densities belong to a ground state, restricts B to a range of values (let us call this the set \mathfrak{R}_0) for which the state with these particular spin densities is the ground state and not some other state (we refer to Refs. 39 and 40 for a discussion of these points):

$$\rho_\alpha, \rho_\beta \rightarrow \begin{cases} \nu(\mathbf{r}) + C | C = -\Delta N g\mu_B B/2N, \\ \mathbf{B}(\mathbf{r}) + B\hat{e}_z | B \in \mathfrak{R}_0. \end{cases}$$

For the set of values $B \in \mathfrak{R}_0$ the energy of the ground state varies, although the energy difference with respect to the fully ionized system (*without spin flips*) remains constant. The excitation energies to other states are, however, not constant over the set of allowed choices $B \in \mathfrak{R}_0$.

Our Kohn–Sham solution for the Li atom illustrates these points. We have in this paper made the natural choice $\nu_{s\alpha}(\infty) = \nu_{s\beta}(\infty) = 0$, in which case the orbital energies can be associated directly with ionization energies. Since $\nu_{s\alpha}(\infty) = C + g\mu_B B/2$ and $\nu_{s\beta}(\infty) = C - g\mu_B B/2$, this implies $C = B = 0$. Unfortunately, with this choice the electron configuration we are using does not correspond to the ground state of the Kohn–Sham system. In order for that to be the case, we need to add a KS effective magnetic field $B\hat{e}_z$ of such strength that $\varepsilon_{2s\beta}$ is shifted upwards with respect to the α levels by 0.48 eV, i.e., $\nu_{s\beta}(\infty) - \nu_{s\alpha}(\infty) = -g\mu_B B > 0.48$ eV. There is also a maximum strength to the B field, since the $1s\beta$ level may not rise above the empty $2p\alpha$ level. At the magnetic field strengths where our electron configuration corresponds to the ground state of the KS system, we can still make, e.g., the α orbital energies directly comparable to ionization energies, by choosing $\nu_{s\alpha}(\infty) = C + g\mu_B B/2 = 0$. Then, however, the β orbital energies cannot be directly compared to ionization energies, but of course the differences with respect to the asymptotic value of the β potential, $\nu_{s\beta}(\infty) = -g\mu_B B$, can be used: $\nu_{s\beta}(\infty) - \varepsilon_{i\beta} \approx I_i^1(\varphi_i^{-1})$.

There is some advantage to using consistently the “natural gauge” $\nu_{s\alpha}(\infty) = \nu_{s\beta}(\infty) = 0$, in view of the meaningfulness of the orbital energies. However, it is unfortunate that there is a danger then that one cannot rely on finding the correct ground state spin densities with an Aufbau configuration of the KS system. This is exemplified by the present case of the Li atom. When the electron spin configuration is known beforehand, as with Li, this is not prohibitive: a good algorithm (density functional) to find the KS potentials from spin up and spin down densities might still allow one to carry out self-consistent KS calculations with $\nu_{s\alpha}(\infty) = \nu_{s\beta}(\infty) = 0$. If, however, the electron spin configuration is not

known, but the calculation is meant to determine it, the unknown strength of the effective Kohn–Sham magnetic field [or equivalently the asymptotic difference $\nu_{s\alpha}(\infty) - \nu_{s\beta}(\infty)$] would be a serious obstacle.

As follows from Table V, the UBP solution does not exhibit features similar to those of the UKS solution. Indeed, the UBP energy of the $2s\beta$ LUSMO of -2.29 eV is 1.98 eV higher than that of the $2s\alpha$ HOSMO, and the electron configuration $(1s)^2(2s\alpha)^1$ obeys the Aufbau principle. The $1s\beta$ energy is slightly higher than the $1s\alpha$ energy, as expected. However, both BP $1s$ energies are quantitatively rather poor; they are much higher than the ionization energies to the triplet state ($\epsilon_{1s\beta} = -I_{H-1}^1 + 12.7$ eV) and the average of triplet and singlet states ($\epsilon_{1s\alpha} = (-I_{H-1}^1 - I_{H-1}^0)/2 + 13.38$ eV), respectively. Finally, due to the well-known upshift of virtual levels in the HF method, the energy of the UHF $2s\beta$ LUSMO of -0.04 eV is much higher than that of the UHF $2s\alpha$ HOSMO.

V. CONCLUSIONS

In this paper the spin-unrestricted Kohn–Sham solution is constructed from the *ab initio* (CI) spin densities ρ_σ for the prototype doublet molecules NO_2 , ClO_2 , and NF_2 with the iterative local updating procedure of van Leeuwen and Baerends. A qualitative justification of the LB procedure is given with a “strong” form of the Hohenberg–Kohn theorem.

The calculated energies $\epsilon_{i\sigma}$ of the occupied KS spin orbitals provide numerical support to the Koopmans-type interpretation of the ϵ - I relations of SDFT. In particular, the energies $-\epsilon_{i\beta}$ of the minor spin (β) valence orbitals of the considered doublet molecules correspond fairly well to the experimental VIPs I_i^1 to the triplet cationic states. The energy $-\epsilon_{H\alpha}$ of the unpaired α spin orbital is equal to the first VIP I_H^0 to the lowest singlet cationic state. In turn, the energies $-\epsilon_{i\alpha}$ of the major spin (α) orbitals of the closed subshells correspond to the average of the experimental VIPs I_i^1 and I_i^0 to the triplet and singlet cationic states. The Koopmans type of theorem produces in the case of unrestricted Hartree–Fock calculations a substantially worse estimate of VIPs and their averages. In the case of NO_2 and ClO_2 it predicts erroneously that the first ionization is not out of the unpaired spin orbital, but out of the highest fully occupied orbital, i.e., to a triplet ion state.

The UKS solution for the Li atom illustrates the nonuniqueness of the Kohn–Sham potentials in SDFT. In the Kohn–Sham calculation with the potentials constrained to go to zero asymptotically, it is found that the empty $2s\beta$ one-electron level is *lower* than the occupied $2s\alpha$ level. The electron configuration thus does not obey the Aufbau principle. The given spin densities, however, do not determine the potentials completely, and a magnetic field in the z direction may be added that does not change the wave function (KS orbitals) and the spin densities, but shifts the β levels up with respect to the α levels so as to restore the *Aufbau* principle.^{38–40} This does not invalidate the interpretation of the orbital energies as approximate ionization energies; one only should take a possible nonzero asymptotic value of the spin potential into account: if $\nu_{s\beta}(\infty) \neq 0$, $\nu_{s\beta}(\infty) - \epsilon_{i\beta} \approx I_i^1(\varphi_i^{-1})$.

The present results and the results of Ref. 5 suggest the spin-unrestricted KS theory as a natural one-electron independent-particle model for interpretation and assignment of the experimental photoelectron spectra of open-shell molecules.

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